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Partitioning of Substrate within Aqueous Micelle Systems by Using Dead-End and Cross Flow Membrane Filtrations

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Abstract

The partition coefficients of different solutes as Itaconic acid (IA), dimethyl itaconate (DMI), diethyl itaconate (DEI) and dibuthyl itaconate (DBI) between water and micelles of Triton X-100 are determined by the two methods of separation namely Cross Flow Filtration and Dead-End Filtration by using a membrane that rejects the micelles and lets passing the molecules of solute. Partition coefficient of the solute between the aqueous phase and micelle aggregate was determined by titration and HPLC methods. The results obtained are discussed in our researcher's group and compared to others made with theoretical data reported from simulation. The effect of the different concentrations of solutes and transmembrane pressures have been investigated using a commercial membrane Nadir C005 (MWCO = 5 kDa).

Keywords; Micelle-enhanced Ultrafiltration, rejection of micelles, partition coefficient in micelles, modelling of distribution of partitioning coefficient.

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Nomenclature

K	[-]	Partition coefficient
XM	[-]	Molar fraction of solute in micelles
XW	[-]	Molar fraction of solute in water
CMC	[mol./L]	Critical micelle concentration of surfactant
CT	[mol./L]	Initial concentration of micelles in volume V0
V0	[L]	Initial volume of solution
n_S^W	[mol.]	Moles of solute in water
n_S^0	[mol.]	Moles of solute in initial volume of solution
n_T^0	[mo.]	Moles of surfactant in total volume (V0)
n_W	[mol.]	Moles of water in initial volume of solution
VP	[L]	Volume of permeate
VR	[L]	Volume of retentate
C_T^R	[mg/L]	Surfactant concentration in retentate
C_T^P	[mg/L]	Surfactant concentration in permeate
Rmembr.	[mm]	Radius of the membrane
Δ P	[bar]	Transmembrane pressure
C_S^M	[mg/L]	Concentration of solute in micelle phase
C_S^W	[mg/L]	Concentration of solute in aqueous phase
C_S^0	[mg/L]	Concentration of solute in initial volume of solution V0
C_T^0	[mg/L]	Concentration of surfactant in initial volume of solution
C_T^M	[mg/L]	Concentration of surfactant in micelle phase
C_T^W	[mg/L]	Concentration of surfactant in aqueous phase
RS	[%]	Rejection of solute in permeate or in retentate
RM	[%]	Rejection of micelles
Δ G	[kJ/mol]	Free energy of the system

1. Introduction

Surfactant solutions which solubilise hydrophobic compounds in aqueous solution have been studied over many years. As a consequent, the partitioning of solutes in these micelle systems is determined in order to evaluate the fraction dissolved in the surfactant. In many cases, the coefficient is not easy to determine by such a technique and depends to several parameters. One of these proposed methods to separate the solute from the retained aggregates is called micelle-enhanced ultrafiltration (MEUF) [1-4]. A simple scheme of the commercial technologies Dead-End Filtration and Cross flow Filtration used in this work is reported in Fig 1.

In the present study, partition coefficients of different solutes as Itaconic acid (IA), dimethyl itaconate (DMI), diethyl itaconate (DEI) and dibuthyl itaconate (DBI) between water and micelles of Triton X-100 are determined by the two methods of separation namely Cross flow and Dead-End Filtration by using a membrane that rejects the micelles and lets passing the molecules of solute. The values of the partition coefficients are compared to those obtained by a mathematical model presented by a collaborated group [5].

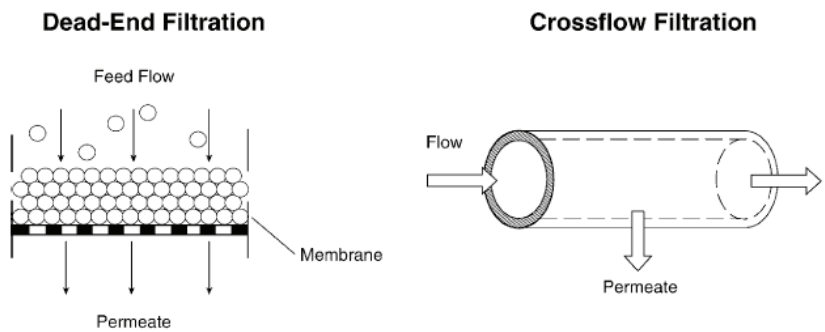

Figure 1. Comparison of conventional "dead-end" filtration with crossflow filtration.

2. Experimental

2.1. Materials and methods

Itaconic acid (IA) was purchased from Aldrich, dimethyl itaconate (DMI) was obtained from Fluka, diethyl itaconate (DEI) and dibuthyl itaconate (DBI) were supplied by TCI Europe nv and Triton X-100 was from Sigma-Aldrich. Toluene, 2-propanol, acetonitrile and water grade for HPLC were purchassed from Carl Roth GmbH + Co. KG.

All the concentrations were performed spectrophotometrically using an UVIKON 810 spectrophotometer from KONTRON Instrument GmbH (λ = 276 nm, T = 25 °C) and two HPLCs apparatus Dionex GmbH with Chromeleon chromatography software (detector UV-Vis with λ = 210/270nm; flux =0,7 mL/min; P =130/150 bar; Injection volume = 10 µL and 60% ACN & 40% H_2O) and P580 LPG high-pressure quaternary gradient pump and

RP-HPLC Agilent 1100 from h&pAgilent (Pumpe G1311A), Entgaser G1379A, Autosampler G1313A, Diodenarraydetektor G1315A, Thermostat G1316A with λ = 210/270nm; flux =2, 0 mL/min; P =150/160 bar; Injection volume = 10 µL and 80% ACN & 20% H_2O). For the two methods a column of 120 RP 18-5 µ at 25° C was used.

The permeate was filtrated under different pressures across a membrane at 25 °C using an ultrafiltration (UF) unit consisting of a cell (stirrer speed 700 U/min) from Bioengineering AG (Wald, Schweiz). The assay were fed with a pressure produced by an HPLC pump 64 (Knauer, Germany) and a second pump from Ismatec, A Unit of IDEX-Corporation (BVP-Z). In addition, the fed solution across the same membrane was performed by using a Dead-End Filtration process mode Berghof Laborprodukte GmbH (Niederdruckzelle GN 10-400).

The membrane used in this work was from Microdyn Nadir C-Series, MWCO 5 kDa with a pure water flux > 25 L/(m^2*h) and a test solute of Dextran T10 (1%). The diameters of this membrane were 67 mm and 76 mm for Dead-End Filtration and Cross Flow-Filtration, respectively. A solution of 0,1 g solute (IA, DMI, DEI or DBI) + 1 g Triton X-100 + 1L H_2O was filtrated across the membrane at different pressures 0,6; 0,8; 1,0; 1,2 bar.

Two different methods were used to calculate the partition coefficients (titration and HPLC). In contrast to the titration method, the different concentrations of initial solution permeate and retentate measured by HPLC were more precise.

3. Results and discussion

The partition coefficient can be written as follows

$$K = \frac{X_M}{X_W} \tag{1}$$

$$X_M = \frac{(1-f_{ex})*n_S^0}{(1-f_{ex})*n_S^0 + n_T^0} \tag{2}$$

$$X_M = \frac{f_{ex}*n_S^0}{f_{ex}*n_S^0 + n_W} \tag{3}$$

The following terms are defined as

$$f_{ex} = \frac{n_S^W}{n_S^0} \tag{4}$$

$$n_T = V_0\,(C_T - CMC) \tag{5}$$

As can be seen in Table 1, the partition coefficient is merely independent of the choice of the filtration technique. It seems that the solute depends strongly to the nature of its bonds in aqueous and micelle phases. The influence of the hydrophobicity of the solute on the partitioning coefficient was reported in Figures 2-3. As is seen in these figures, K has an exponential form and depends clearly with the hydrophobic compounds in the micelle systems, from itaconic acid (IA) to dibuthyl itaconate acid (DBI). As a result, more hydrophobic solutes are strongly bound to micelle molecules relating to the rejection in ultrafiltration. In addition, the variation of the transmembrane pressure has no influence on the variation of partitioning coefficient.

The plot of the partition coefficient calculated from both experiment and simulation is shown in Figure 4. To compare the simulated values of K with our data, the following protocol has been considered:

Variation of the different concentrations

a) $C_S^M = f\left(C_S^W\right) \Longrightarrow$ Mathematical equation

b) $K = f\left(C_T^0\right) \quad for \neq \left[C_S^0\right] \Longrightarrow$ Mathematical equation

c) $C_S^M = f\left(C_T^W\right);\ C_S^M = f\left(C_T^M\right);\ C_S^W = f\left(C_T^W\right);\ C_S^W = f\left(C_T^M\right)$

$\Longrightarrow$ Mathematical equations

d) $R_S = f(K); \qquad R_M = f(K)$

$\Longrightarrow$ *Mathematical equations*

$\Longrightarrow$ Final mathematical model

Variation of the free energy

a) $\Delta G = -R * T \ln K$

b) $\Delta G = f\left(n_{R-CH3}\right)$

a) 3 .3.Study of the micelle solutions

b) study of the added chemical components

c) effect of pH

d) shapes of micelles and their implication

Repeat the same experiments with different solutes and surfactants

Table 1. Partition coefficients of Dead-End and Cross Flow Filtrations

Dead-End Filtration		Cross Flow Filtration
Solute	K_{ave}	K_{ave}
IA	2874	2746
DMI	4136	5234
DIE	6946	7524
DBI	42194	48512

K_{ave}: Average value of the partition coefficient

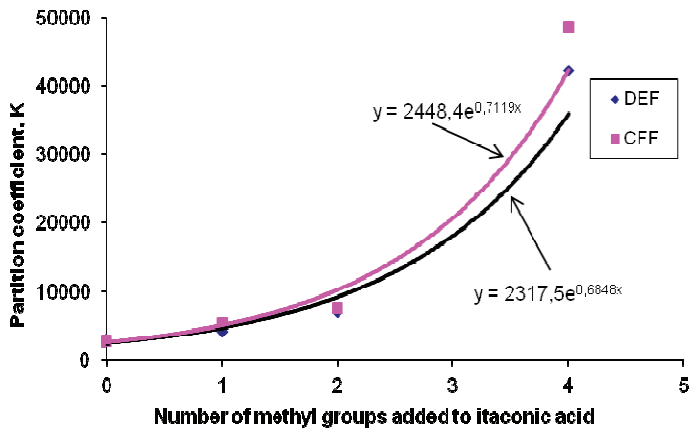

Figure 2. Partition coefficient as a fonction of the methyl groups added to itaconic acid

DEF : Dead End Filtartion
CFF : Cross Flow Filtration

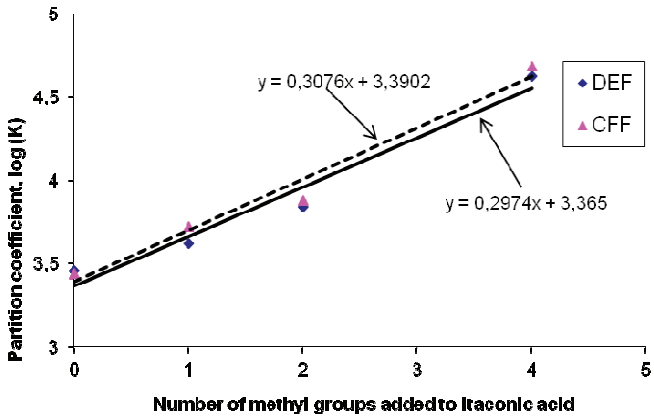

Figure 3. Partition coefficient as a fonction of the methyl groups added to itaconic acid

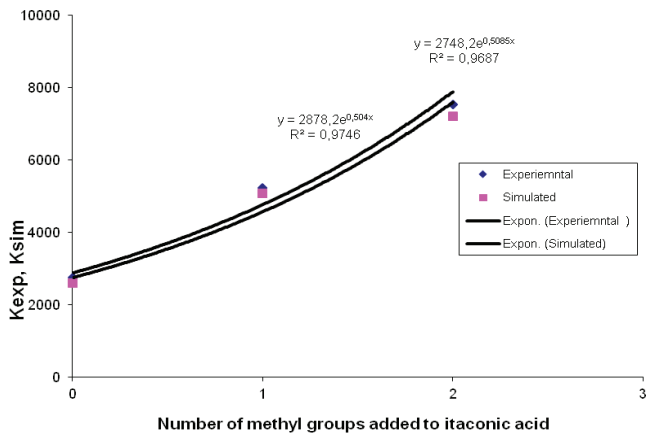

Figure 4. Experimental and simulated partition coefficient as a fonction of the methyl groups added to itaconic acid

Kexp: Experimenta K

Ksim: Simulated K

4. Conclusions

Partition coefficient of micelle system was investigated by increasing the hydrophobicity of the solute and varying the concentration of surfactant and solute. The choice of Dead-End and Cross Flow Filtrations and the variation of transmembrane pressure had no influence on the partitioning coefficient. Micelle enhanced ultrafiltration is a good method used in this work to separate permeate with the solute. Also, the rejection of surfactant was quite high. The comparison of our results with those simulated was in agreement.

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References

[1] ScamehornJ. F., S. D. Christian, R. T. Ellington, Surfactant-Based Separation Processes, Dekker, New York (1989)
[2] Keskinler B., U. Danis, A. Cakici, G. Akay, Sep. Sci. Technol., 32 (1997), 1999
[3] Schwarze M., R. Schomäcker, Chem. Ing. Tech. 78 (2006), 7, 931
[4] Schwarze M., M. Djennad, A. Rost, M. Buggert, W. Arlt, R. Schomäcker, Chem. Ing. Tech. 78 (2006), 9, 1277
[5] Buggert M., L. Mokrushina, I. Smirnova, R. Schomäcker, W.Artl, Chem. Eng. Technol. 29 (2006), 5, 567